

**THE USE OF A DIAPHRAGM COUNTERCURRENT
ELECTROMIGRATION APPARATUS TO SEPARATE THE
RARE EARTHS AND TO CONCENTRATE ISOTOPES
IN AN AQUEOUS MEDIUM**

**DISSERTATION SUBMITTED FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY**

**to the
PHILOSOPHICAL FACULTY SECTION II
of the
UNIVERSITY OF ZURICH**

**by
Ernest Robert Ramirez
from Chicago, U. S. A.**

**Approved by
Prof. Klaus Clusius**

**Juris-Verlag Zurich
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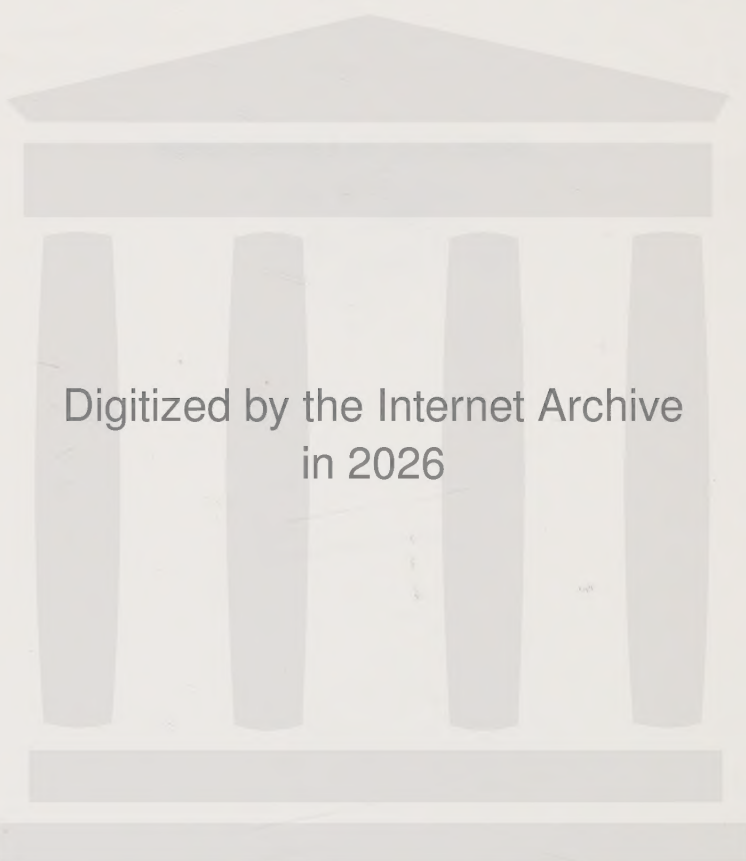
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Dedicated to my beloved parents



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AKNOWLEDGEMENTS

I am indebted to Prof. K. Clusius for supplying the larger Part of the rare earths used. I am most thankful to him for his stimulating ideas and ever guiding assistance.

I am obliged to Dr. H. Hintenberger from The Max Planck Institute of Chemistry at Mainz, Germany, for the analysis of the Rubidium and Lithium isotopes.

May I express my deepest gratitude to "THE TRENNBOY CLUB" of P.C.I. for making my stay at the university a pleasant one.

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ABSTRACT

A method of diaphragm countercurrent electromigration is described. The method uses a diaphragm packing. The countercurrent stream is automatically controlled by conductivity cells. The apparatus requires very little attention or re-adjustment.

Voltages of 600 and 2500 have been used. The results on the absolute separation of alkali metals and also on the absolute separation of the rare earth metals are given. The results on the concentration of ^{85}Rb in rubidium and of ^6Li in Lithium are tabulated.

INTRODUCTION

A close study of separation processes indicates that in order to be able to separate two or more mixed substances, there must first be a difference in at least one of their physical or chemical properties. Once this difference is found, then a means for the concentration or for the absolute separation of the substance becomes a much simpler problem.

The idea to use differential mobility of the ions as a physical means to separate isotopes in solution was first put forth by Lindemann (1). The first successful attempt to use differential mobility as a means of concentrating isotopes was carried out by A. Klemm (2) in 1944. Klemm was able to enrich the lighter isotope of silver by means of countercurrent electrolysis of silver iodide.

Even in 1944, it was generally accepted that a separation of isotopes in an aqueous solution, was not probable, as it was assumed that the hydrated isotopes possessed negligibly small differential mobilities.

In 1947, Brewer (3) and coworkers published the first paper on a successful method of concentrating the lighter potassium isotope by differential mobilities in an aqueous solution.

Since 1947, differential mobilities and differential migration properties have been considerably investigated. The method of chromatographic separation, which in the past four years has been so helpful, really in principle depends upon differential migration of solutes through a polyphase system. The migration is effected by a flow of solvent.

Strain (4) and coworkers, in recent years have done much work on electrochromatography. This method uses both the migration of the solute as well as the differential mobility of the ions. The method has been successfully applied to analytical work. Qualitative separation of organic and inorganic ions have also been carried out by two and three way electrochromatography (5).

Hausheer (6) and Bühler (7) have made doctoral dissertations on the separation of ions by countercurrent electromigration.

THE PRINCIPLE AND THEORY OF DIAPHRAGM COUNTERCURRENT ELECTROMIGRATION AS APPLIED TO THE SEPARATION OF IONS

The principle and theory of the process have already been well described by Hausheer (6), Bühler (7) and Brewer (3).

The overall principle of the process under ideal conditions is that the flow of the countercurrent stream is uniform and faster than the heavier ion but slower than the lighter ion. Under these conditions, the heavier ion will be slowly carried with the countercurrent stream, while the lighter ion will gradually work its way toward the cathode section. Theoretically the process is in equilibrium when the velocity of the countercurrent stream is equal to the velocity of the lighter ion. Actually, equilibrium is reached when the back diffusion is equal to the separating rate of the process.

Brewer and coworkers, have almost fulfilled these ideal conditions with their packing of ottawa sand or that of absorbent cotton. However, thermal convection had upset the so called ideal conditions. As a result of this, the separating process was far from satisfactory. Since energy (potential gradient) must be applied to the apparatus, and since the apparatus must be cooled if it is to be kept at a determined temperature, then it follows, that thermal convection currents must exist in spite of the precautions taken.

Our new approach made to solve the problem was to harness these convection currents, and to have them aid in the ion separation rather than upset the process of ion separation. In order to do this, it was necessary to entirely change the nature of the packing. Instead of using the conventional solid packings, which often had taken up as much as 70% of the apparatus volume, (which were also poor heat conductors) we had decided to use semi-permeable membranes. These diaphragms took up only a fraction of a percent of the apparatus volume. The difficulty of channeling which is so critical in the case of solid packings, does not hardly exist in the case of a diaphragm packing. By channeling it is meant that the countercurrent flow of the stream is not uniform, but is restricted to a selected part or parts of the available space rather than being evenly distributed.

It is likely that the mechanisms of the separating process is in some way related to the packing used. Packings such as glass beads, silicon carbide and sand do not have the same mechanisms of separation as does the diaphragm packing. It has been observed that while thermal convection currents are

harmful in the case of solid packings, they are definitely beneficial in the case of diaphragm packing.

In a diaphragm packing, the ionic velocities are approximately uniform, throughout the apparatus. The absolute liquid velocity at any point varies considerably. The liquid (countercurrent flow) velocity is a maximum as it passes between the apparatus walls and the periphery of the diaphragms. It is a minimum somewhere between the diaphragms. Slow thermal convection between the diaphragms apparently rearranges the ions in each diaphragm cell such that the faster ions which are brought into a given cell, are not permitted to leave the cell directly without being at least in part exchanged with the slower ions which already were in the cell.

The design of the diaphragm packing is such that the direction of thermal convection is permitted only in a direction which is perpendicular to the ionic migrating path. This tends to lessen any harmful effects which may accompany the thermal convection currents.

Uneven distribution of the potential caused by un-uniform ionic concentrations, create localized heating where the ionic concentration is lower. Such irregularities are self-adjusting in a diaphragm packing. There is also no problem of having entrapped gasses in the packing, or of having a non-uniform packing.

The mechanisms of separation involved in a diaphragm packing are very complicated. It has not yet been possible to develop a mathematical expression which would follow through the process. However, if one assumes the ideal case where the absolute point velocity of the ions is equal to the absolute point velocity of the countercurrent stream, then the rate of separation of a binary mixture may be given by the following differential equation.

$$\frac{d (\ln Q)}{dt} = \frac{A P}{V_c L} (\mu_1 - \mu_h) \quad (1)$$

If the quotient $\frac{A P}{V_c L}$ be replaced as being the cell constant then the equation may be written as shown in 2.

$$\frac{d (\ln Q)}{dt} = K (\mu_1 - \mu_h) \quad (2)$$

Where; Q is the separation factor. This is the quotient of the ratios of the two ions in the cathode and in the anode section respectively.

A is the cross-sectional area of the apparatus.

L is the length of the apparatus.

P is the potential drop across the entire apparatus.

t is the time.

μ_1, μ_h are the mobilities of the light and heavy ions respectively.

V_c is the volume of the cathode compartment.

C_{il} is the initial concentration of the light ion.

C_{ih} is the initial concentration of the heavy ion.

C_T is the total concentration of both ions.

A material balance of the separating system at any point is also a means of following through the separating process. The material balance only takes into account the ions which enter a given point as a result of their electromigrating velocity and ions which leave the point as a result the countercurrent stream. The effect of back diffusion is not considered in this material balance. Likewise the effects of thermal convection and turbulence are overlooked. This balance assumes the ideal conditions that the point liquid velocity is equal to the point ionic velocity. A material balance of a binary system is expressed in equation no. 3.

$$\Delta C_1 V_c = K'' A C_{il} \left(\frac{P}{L} \mu_1 - V_s \right) \Delta t \quad (3)$$

But the velocity of the countercurrent stream V_s is the average velocity of both ions at that point.

$$V_s = \frac{P}{L} \left(\frac{C_{il}}{C_T} \mu_1 + \frac{C_{ih}}{C_T} \mu_h \right) \quad (4)$$

Upon substituting equation 4 in equation 3 the following simplification can be made.

$$\Delta C_1 V_c = K'' C_{il} \frac{A P}{L} \left[\mu_1 \left(1 - \frac{C_l}{C_T} \right) - \mu_h \frac{C_h}{C_T} \right] \Delta t \quad (5)$$

The cell constant of the apparatus is given by K'' .

Although the material balance given by equation 5 is very helpful, and easy to use, it is nevertheless much to be criticized from the chemical point of view. The equation is approximately correct only at infinite dilutions, when the ion concentration of the solution is equal to the solute concentration. The equation also holds only for relatively small values of time. That is to say much before the time of equilibrium.

CALIBRATION AND DESIGN OF A COUNTERCURRENT APPARATUS

The time necessary to investigate all the possible variables in the design of a diaphragm packed apparatus was far greater than was possible to be given to this problem. Thus, only a few of the variables which were thought to be most important were investigated. In all the experiments, dialysis paper was the material used to prepare the diaphragms.

The general set-up of the apparatus, with exception of an automatic control, and a few other small changes, has been described by Bühler (7). Essentially it consists of a separating tube or trough where the ions are migrating under a potential gradient. The anode and cathode sections are at the opposite ends of the tube. A packing consisting of semi-permeable diaphragms lies between the anode and cathode. By means of a pressure cell, water (or a water solution) is fed dropwise into the cathode section. This water flow is in the opposite direction of the migrating cations. The water is drawn off at the anode section by a constant level siphon. This flow of water from the cathode section to the anode section is called the countercurrent stream.

An automatic regulating device which controls the current in the pressure cells is a conductivity cell, located in the cathode section. The pressure cell is connected in series with the conductivity cell. The cells are so designed that the potential drop across the pressure cell is negligibly small when compared to the potential drop across the conductivity cell. The pressure cell consists of two closely spaced platinum foils in a concentrated solution of lithium hydroxide. As a current passes through the cell, gas (hydrogen and oxygen) is evolved at both platinum electrodes. This gas in

turn exerts a pressure on the water lever in the countercurrent reservoir which forces out an equivalent amount of water from the countercurrent reservoir. See figure I.

Diaphragm electromigration apparatus

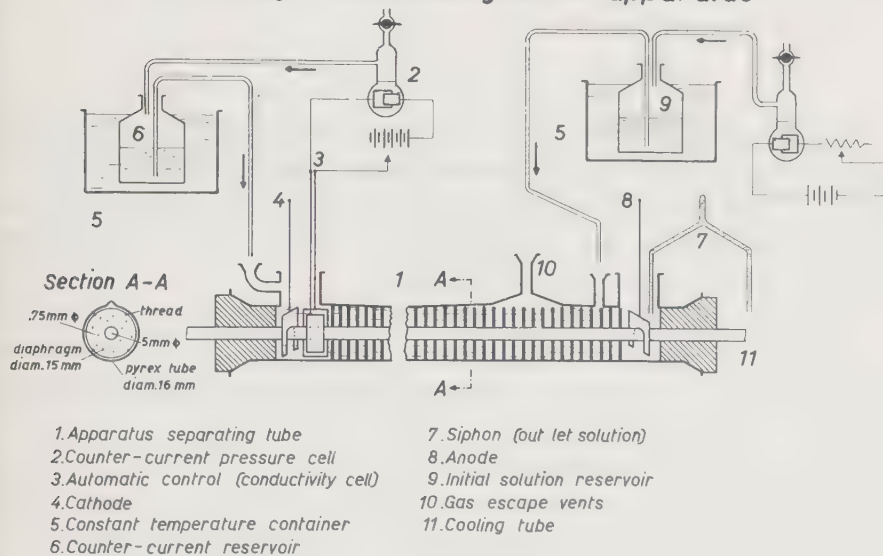


Fig. I

General details

Unless otherwise specified, the separating apparatus was a pyrex tube 1.6 cm (I. D.). The tube had gas escape vents at about every 10 cm of tube length. (see fig. I.) The top part of the glass tube was slightly blown out to allow a slow upward taper toward the gas escape vents.

The diaphragms were made of dialysis paper and were punched out with a cork borer to have a diameter of 1.55 cm. The center of each diaphragm had a hole of 0.50 cm. The diaphragms were strung up on a glass tubing having an o. d. of 0.5 cm. They were equally spaced anywhere from .5 to .25 cm apart. To make sure that the diaphragms maintained their proper

spacing during the experiment, they were sowed together (with a needle and thread) as originally spaced. The .5 cm tubing together with the sowed diaphragms were then pushed into the separating tube (1.6 cm). The apparatus was cooled by running water through the .5 cm inner tube. Air cooling on the outside also had some cooling effect.

Choice of cations and method of analysis

The sodium and potassium cations were selected as having many advantages. The fact that the differential mobility of these two ions is quite large, offers the possibility of being able to carry out short time experiments (50 hrs.), from which much information can be obtained. These ions are also no depositable under the operating conditions.

A flame photometer was used to determine the absolute concentration of the two cations in solution. This method of analysis, besides being very accurate, also had the advantage of using only very small quantities of the substance. The analysis was run using cation concentrations in the neighborhood of 0.001 N. This was very important because the taking of samples from the apparatus did not appreciably alter the conditions in the separating tube. In most cases 1 cc of sample were taken. The taking of samples was not only limited to the cathode section. They could be taken anywhere along the separating tube.

THE EFFECT OF CONVECTION ON THE SEPARATING FACTOR

This first series of experiments were designed to determine whether thermal convection influenced the separation process, and if so, to what extent. In order to follow through the effects of thermal convection, three experiments were designed which had varying degrees of thermal convection.

The first experiment was made to unfavour thermal convection. This was accomplished by making the separating apparatus thin (.8 cm wide) but tall (3 cm high). The cooling surface was large and the heat conducting properties of the material were poor. A plexi-glass wall .2 cm thick was used. The cooling was done along the sides of the plexi-glass trough. See figure III.

In the second experiment it was desired to encourage thermal convection. In this experiment, the cooling area was reduced by about a factor of 4, and a better heat conductor was used (thin glass tubing). The cooling was done in the center of the electrolysed solution. The water flow through the tube was very fast. This considerably reduced the film coefficient on the cooling water side and maintained a much cooler surface than in the case of the plexi-glass walls.

In the third experiment, a circular pyrex-tube (1.6 cm i.d.) was used as the electrolysing apparatus instead of the high narrow trough. Again the cooling was done in the middle of the solution. The circular form of the tube assisted the convection currents by conforming with the shape of the currents.

In each case the apparatus was filled with a hydroxide solution of sodium and potassium. The ratio of potassium to sodium was 0.06. Water was fed in at the cathode section. The initial solution reservoir maintained a potassium to sodium ratio of 0.06 throughout the experiment. This reservoir constantly supplied the anode section with fresh ions.

Apparatus set up to unfavor thermal convection

A plexi-glass trough was packed with diaphragms which were evenly spaced at .5 cm apart. The trough was 50 cm long, .8 cm wide and 3 cm high. The diaphragms were cut to the dimensions of .78 cm. X 3 cm. Each diaphragm had 10 holes (.075 cm) randomly made over its surface. These holes were made to assist a smooth flow of the countercurrent stream. The solution level was maintained at 2.5 cm. The plexi-glass trough was cooled on its sides. The cooling surface was so large that thermal convection currents were not favored.

Apparatus set up to encourage thermal convection

The same plexi-glass trough was used. Instead of cooling the trough on its sides, it was cooled by a .4 cm (o.d.) glass tubing which ran slightly above the middle of the liquid level. The same dialysis paper was used as in the previous experiment. However, in this case the diaphragms had a .4 cm hole bored 1.5 cm from the bottom end. The 10 holes .075 cm, were

also randomly made in the diaphragms. The diaphragms were then strung up on the glass tube and sowed together to a spacing of .5 cm. The packing together with the glass tubing were then fitted into the plexiglass trough.

Apparatus set up to encourage and assist thermal convection

Thermal convection currents in pure liquids and gasses are caused by a temperature gradient which induces differential density regions. These differential density regions cause the fluid to flow in an oval path traveling from the hot body to the cold one.

It had been decided that in order to assist thermal convections, the apparatus should be circular. This shape would conform to the convection currents and thus enhance them.

A pyrex tube 1.6 cm i.d. was used. Circular diaphragms 1.55 cm in diameter with a .5 cm hole in their center were prepared. Ten .075 cm holes were randomly made on the diaphragm surface. The diaphragms were then strung up on the .5 cm glass tube and were sowed to maintain a spacing of .5cm. The glass tube, together with the diaphragms were then pushed into the separating tube (1.6 cm i.d.). The length of the separating tube was 50 cm.

The results of these three experiments are shown in figure II. The operating conditions are shown in table I.

Cross-sectional views of Apparatus

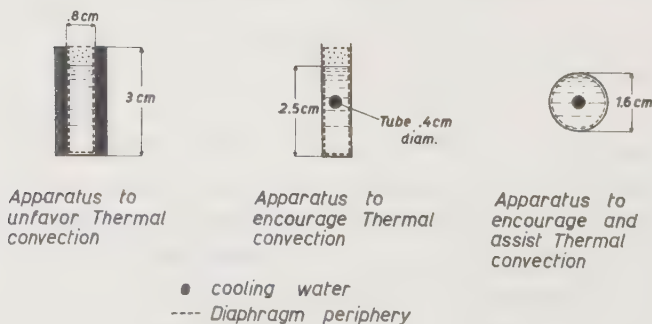


Fig. III

OPERATING CONDITIONS IN THE THERMAL CONVECTION EXPERIMENTS

Table I

	Av. cell Temperature	Av. cell current	Av. stream volume	volts	App. area
App. to unfavour thermal convection	42°C	140 m.a.	65 cm ³ /hr	600	2 cm ²
App. to encourage thermal convection	40°C	138 m.a.	63 cm ³ /hr	600	1.9
App. to encourage and assist thermal con- vection	39°C	136 m.a.	62 cm ³ /hr	600	1.8

The ionic concentration in each experiment was about 0.015 N.

Effect of thermal Convection on the separating factor.

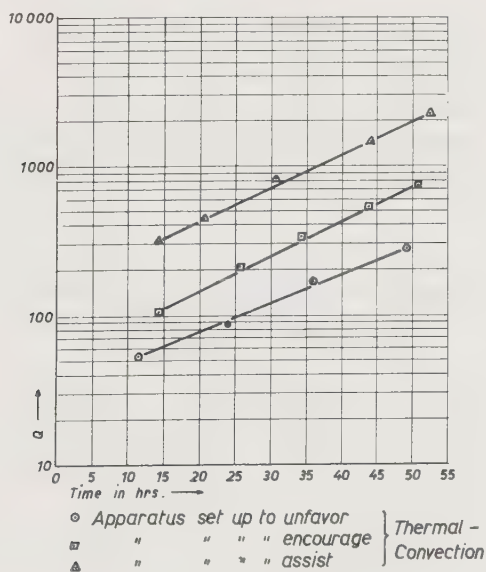


Fig. II

From the results shown in figure II, it can be surely said that thermal convection which takes place in a direction perpendicular to the ionic migrating path, does considerably improve the separating process. There is no possibility that either experimental errors or operating conditions could account for the marked difference in the separating rates. At worst the experimental results are reproducible to ± 10 percent. The experiments have been run in duplicate.

The enormous difference in the results of the three experiments can only be accounted for by the different degrees of thermal convection. A close study of the diaphragm packing confirms the fact that convection currents perpendicular to the ionic migrating path are helpful.

Separation factor as a function of the number of diaphragms

It has already been shown that cations can be separated by use of a diaphragm packing. The question arises, just what part do the diaphragms play in the separation. It is also interesting to determine whether the diaphragms are completely responsible for the separation.

A series of three experiments have been carried out by varying the number of diaphragms used in a given apparatus. Experiments with diaphragm spacings of .08, 1, and 2 diaphragms per cm have been tried.

The plexi-glass trough described under "Apparatus set up to unfavour thermal convection" was used in all three runs. The first experiment used only four diaphragms. One diaphragm was placed before the anode section, another just before the cathode section. The other two were equally distant spaced in the middle of the apparatus. This spacing gives an average of 0.08 diaphragms per cm.

In the second experiment 48 diaphragms were used. They were evenly spaced one cm apart.

In the third experiment, 96 diaphragms were employed. The diaphragms were evenly spaced at .5 cm.

The general operating conditions in all three experiments were maintained approximately the same. The cell current was 140 ± 10 m.a.

The cell temperature was $40 \pm 5^{\circ}\text{C}$. The counter current stream was $60 \pm 5 \text{ cm}^3$ per hour and the ratio of potassium to sodium in the anode section was kept at .060. The ionic concentration in the electrolysing cell was .015 N. A voltage source of 600 v was used.

The results of these three experiments are shown in figure IV. It may be concluded that the diaphragms are entirely responsible for the separation. However, it does not follow that the more diaphragms an apparatus has, the better will be its separating power. There is an optimum spacing distance, beyond which an increase in the number of diaphragms does not appreciably add to the separation power of the apparatus. It should be noticed that in the experiment with 48 diaphragm, the separating factor is very similar to that of 98 diaphragms. However, when only 4 diaphragms were used, the separating power of the apparatus was unquestionably bad.

*Separation factor as a Function
of Number of Diaphragms.*

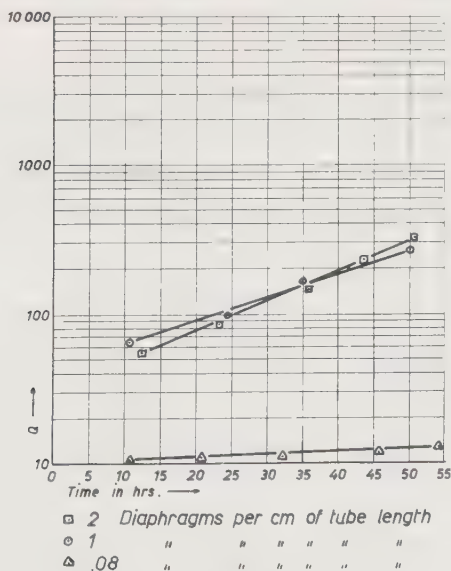


Fig. IV

Separation factor as a function of the tube length at a constant voltage

Equation no. 1. indicates that the rate of separation for a constant voltage source logarithmically increases as the tube length is shortened. A series of three experiments have been carried out to test the practical validity of this equation.

The apparatus used for this group of experiments has already been described under, "Apparatus set up to encourage and assist thermal convection". A drawing is shown in figure I. The length of the apparatus was varied from 14 to 46 cm. A constant voltage source of 600 volts was used.

It was desired to maintain the cell current and the temperature in each of the three experiments approximately constant. As a result of this restriction the concentration of the ions in each experiment was varied. Tube lengths of 14, 20.5 and 46 cm were tried. For the 14 and 20.5 cm apparatus, inside cooling proved to be insufficient. These two tubes were also cooled on the outside by tap water. The apparatus 46 cm long was cooled only by the inner cooling tube.

The shorter the apparatus is, the greater is the potential drop per centimeter length. This also corresponds to a greater ionic velocity. However, since the velocity of the countercurrent stream must be equal to the average velocity of the ions, then it follows that the countercurrent stream volume must be greater for shorter tube length. This is clarified in table II.

Table II

Operating conditions for the experiments of varying the tube length

Tube length	Av. cell current	Av. cell temperature	Av. stream volume	Volts/cm	No. of diaphragms	conc.
46 cm	180 m.a.	44°C	93 cm ³ /hr	13	120	0.015 N
20.5 cm	185 m.a.	37°C	157 cm ³ /hr	28.5	60	0.011 N
14 cm	190 m.a.	39°C	205 cm ³ /hr	43	40	0.008 N

*Tube length as a Function
of the Separation factor.*

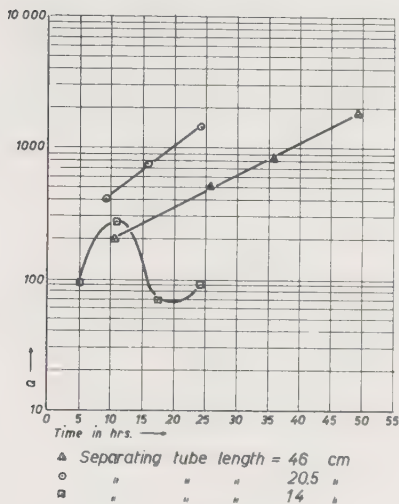


Fig. V

The results of these three experiments are shown in figure V. It may be concluded that the shorter apparatus, generally do yield faster separations. This is in accord with equation no. 1. However, there is a critical length below which the separating process becomes drastically unstable. From figure V, it can readily be seen that the 20.5 cm apparatus did have a greater separating power than the 46 cm apparatus. But when the separating tube was made only 14 cm long, the apparatus became completely unstable. Whether the countercurrent stream was too fast or whether the automatic control was not sensitive enough is difficult to say. Nevertheless the results of the 14 cm apparatus were unsatisfactory. This experiment with the 14 cm tube was repeated. Again sporadic separation factors were obtained, confirming the fact that this separating tube was not suitable.

Under the conditions of this experiment the optimum tube length lies in the neighborhood of 20 cm. This corresponds to a potential drop of about 30 volts per cm.

Separation factor as a function of the temperature

The separation of potassium from a sodium-potassium mixture has been carried out at two temperatures. The ratio of potassium to sodium in the anode section was .06. The two experiments were carried out in a pyrex tube apparatus, which had a length of 46 cm. In both experiments 110 diaphragms were employed. The operating conditions for these two experiments are given in table III.

Table III

Operating conditions for the determination of Q at two temperatures

Length of apparatus	voltage	Av. temp.	Conc. of ions	Cell current
46 cm	600	60°C	0.011	180 m. a.
46 cm	600	35°C	0.015	175 m. a.

The results obtained in these two experiments are shown in figure VI. It is difficult to precisely evaluate the results of the two experiments. At first glance, it appears that the separation is better at 60°C. However, it must not be forgotten, that in the case of the 60°C experiment, the ion concentration is lower than in the 35°C run. Since the transport (cell current) is about the same in each case, then it should be expected that the separation factor would be higher. Another influence of the higher temperature which has to be considered is the smaller hydration of the ions. This means that the separation factor increases with rising temperature. From the standpoint of back diffusion, the separating process should be more efficient at the lower temperature, but obviously the other influences are much greater than back diffusion. Contrary to what would be expected, it seems to be advantageous to work at elevated temperatures. This is encountered also in other separation processes like chemical exchange.

*Effect of Temperature
on separating factor.*

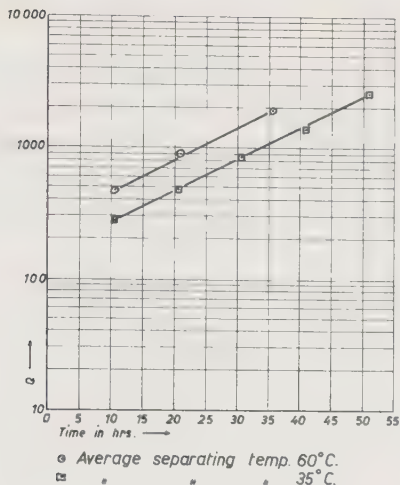


Fig. VII

Conclusion from the calibration and design of an electromigration apparatus

1. The design of an electromigration apparatus should be such that thermal convection be permitted in a direction perpendicular to the ionic migrating path.
2. For an apparatus which is 1.6 cm in diameter, the optimum diaphragm spacing lies between .5 cm and .25 cm.
3. In the case of potassium and sodium, higher temperatures do increase the rate of separation.
4. In the case of potassium and sodium, an apparatus length which corresponds to 30 volts/cm was found to be the optimum.

RESULTS ON THE ABSOLUTE SEPARATION OF POTASSIUM FROM SODIUM BY COUNTERCURRENT ELECTROMIGRATION

All the experiments to this point have used only a 600 d.c. source. When the change was made from 600 to 2300 volts, a much larger apparatus was necessary. The true purpose of this experiment was to calibrate the new apparatus, and to see that it functioned properly. This was done with the intention of using the same apparatus for the separation of isotopes at some later date.

The apparatus was a pyrex tube, one meter long and packed with 250 evenly spaced diaphragms. A new d.c. voltage source was constructed. This source used the three phase 500 volt line as the input and delivered 2300 volts d.c. at the output. The day and evening voltages varied by about 150 volts. The week end voltage were often 250 volts higher than the day voltages. Although this variation of voltage is undesirable, it was observed that this in no way interfered with the separation process. The automatic countercurrent control which was regulated by a conductivity cell, handled these fluctuations very nicely.

The apparatus was filled with a 0.012 N sodium-potassium hydroxide solution. This solution as well as the initial reservoir solution had a potassium to sodium ratio of 0.01. All the previous experiments used a ratio of 0.06. The operating conditions for this experiment are shown in table IV.

Table IV

Operating conditions in the potassium-sodium separation

$\frac{K^+}{Na^+}$	initial	Av. temp.	Av. cell current	Av. stream flow	Av. voltage	volts/cm
0.01		65°C	180 m.a.	240 cm ³ /hr	2300	23

The experiment was run over a period of about one week. Frequent samples were taken along the tube length. Time separation curves as a function of the tube length are shown in figure VII. It is admitted that not

Separation of potassium from sodium with 2500 volts

ratio of $\frac{K^+}{Na^+}$ in anode reservoir = .01

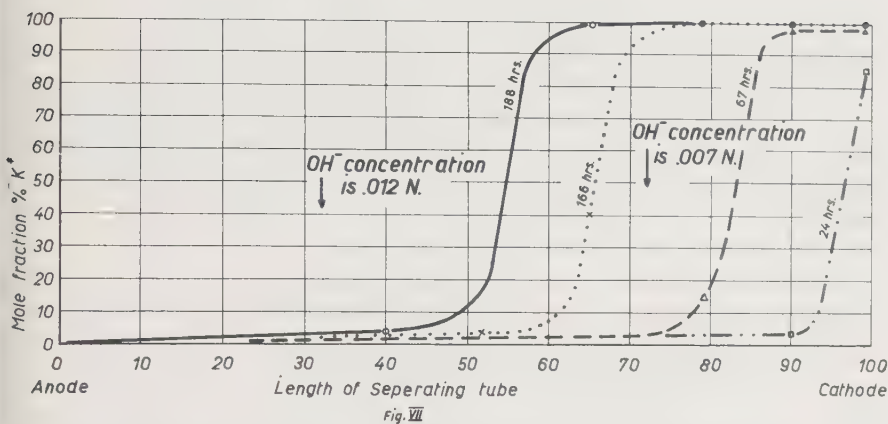


Fig. VII

enough analysis were made along the separating tube length to give a very precise time-concentration curve in this experiment. However, it is felt that sufficient points are given to show curves with an unmistakable trend. It is this trend which carries the valuable information. It should be noticed from figure VII, that the slopes of the time-concentration curves are very steep. From a theoretical standpoint, the slopes of the curves are a function of the differential mobilities of the ions, the potential drop per cm and finally the adverse effects of back diffusion and random convection mixing. The curves indicate that the undesired effects of the two latter processes have been kept at a minimum. The satisfactory results obtained in this experiment do offer promising attempts to concentrate isotopes in an aqueous solution.

Since the separation process can be rather well followed in figure VII, it has been decided to use this figure to test the equation for the material balance. It should be remembered that equation no. 5 is valid only for times much before equilibrium. Under these conditions it should apply to all the time-concentration curves that have been plotted, since these are quite far from equilibrium. (See page 13). The mobilities of potassium and sodium ions can be found in most handbooks. Their values are shown below.

Mobility in water at 18°C for infinite dilution.

Potassium ion 6.7×10^{-4} cm²/sec.

Sodium ion 4.5×10^{-4} cm²/sec.

By using the above mobility values, and the observed results from fig. VII, it is possible to calculate the cell constant K" which corresponds to the efficiency of the separating process, for the said apparatus. The results of such a calculation are shown in table V.

The mobilities of the ions should be corrected for the temperature of the experiment. A rule of thumb which is approximately correct is that the mobility of an ion increases about 2% for each degree centigrade. In calculating table 5 this general rule was used.

Table V

Efficiency of the separating process

Time	Observed enrichment* of K in apparatus (in mill-moles)	Calculated** enrichment (in mill-moles)	Cell Constant K"	Process eff. in per cent.
24 hrs.	.1	.21	0.47	47 %
67 hrs.	.24	.56	0.42	42 %
166 hrs.	.58	1.42	0.41	41 %
188 hrs.	.68	1.61	0.42	42 %

* These values were obtained by integrating the area under the time curves shown in figure VII.

** By using the right hand side of equation no. 5 (see page 13), the theoretical enrichment of the apparatus could be calculated.

In conclusion, it has been shown that the separation process with the diaphragm packing is about 42% efficient. Such an efficiency is considered to be rather good. However, it is felt that the efficiency might still be improved by making some modification in the cell design.

THE ABSOLUTE SEPARATION OF RARE EARTHS BY THE DIAPHRAGM ELECTROMIGRATION METHOD

Introduction:

The problem of separating the rare earth metals is an old one. The difficulties involved in this problem are many. Methods such as fractional crystallisation, solvent extraction, valence change and ion exchange have all been tried. Although each method has definite advantages for the separation of a certain few, none of these methods can be used for a complete separation of all the rare earths.

The first attempt to prove that the rare earths do have appreciable differential mobilities in aqueous solutions was carried out by Kendall and Clarke (8) in 1925. They used an agar-agar packing in their experiment. The reason for their choice of an agar-agar packing was to minimize the adverse effects of back diffusion and mixing convection currents. By the process of differential mobilities they were able to show a definite shift in the composition of a binary rare earth mixture.

The behaviour of rare earth metals in an aqueous electromigration cell

When a rare earth chloride or nitrate solution is electrolyzed between two platinum electrodes, a precipitate (presumably the hydroxide) is formed on and around the cathode. This precipitate can be avoided if an acid is dropwise added immediately to the cathode or the cathode section. From the literature (9) it is shown that the rare earth metals in their normal tri-valent state precipitate as hydroxides between pHs of 6-8. It follows that this precipitate can be prevented from forming if the pH of the solution in the cathode section is maintained below a value of 6.

In all the previous experiments where cations were separated, a hydroxide anion was used. In the case of the rare earths, it is necessary to select another anion. The chloride and the nitrate have been tried with rather unsatisfactory results. It was observed, that these anions functioned properly only when a very close control was kept over the experiment. A

small excess of the anion (in form of its respective acid) in the cathode section, brought the pH of the solution to less than 1. This low pH caused the hydrogen ions to conduct the larger part of the current and thus washed back the rare earth toward the anode section. This resulted in an un-uniform rare earth concentration throughout the apparatus. The automatic control (conductivity cell) did not function properly under these conditions. Not enough of the anion caused local precipitation of the rare earths on and around the cathode.

From the theoretical stand point, it would be advantageous to carry out the separation at a pH of 7. At this pH the hydrogen ion concentration is insignificantly small and its presence would not appreciably effect the conductivity of the solution. The fact that the rare earths are not soluble at this pH, necessitates the use of lower pHs.

In order to avoid having fluctuations in the hydrogen ion concentration, it has been decided to work in a buffered solution. It was desired not to work too close to the limiting pH of 6, while near this pH there is the risk of precipitating part of the rare earths. A pH of 4 was considered to have many advantages. Under these conditions, the acetate buffer was found satisfactory. It has been found that the optimum operating conditions are approached when the acetate concentration in the countercurrent flow is 3 times greater than the concentration of the rare earths in the apparatus.

Conductivity measurements of the rare earths

The conductivity measurements of the rare earths at varying concentrations have been published. Spedding (10) et al. have found that the conductivity of the rare earth ions decrease from La. to Yb. respectively. The decrease of conductivity is very pronounced from Nd. to Yb. The results of Speddings work are shown in figure VIII. From this work it might be expected that the separation of the heavier rare earths should be much easier than the separation of the rare earths at the more basic side near to the Nd.

Analysis of rare earths

In all cases the analysis of the rare earths were made by using the absorption spectrum of the respective ions. This method of analysis is described in detail by Moeller (11).

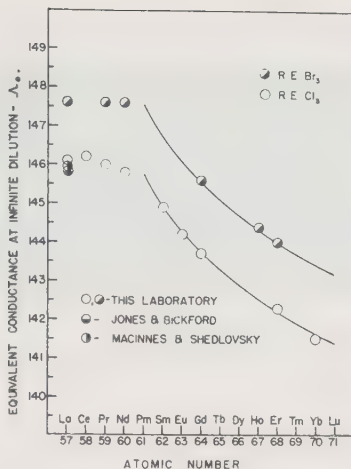


Fig. 2.—Equivalent conductances at infinite dilution for aqueous solutions of rare earth halides at 25°.

Figure VIII

(Taken from the work of F. Spedding)

In each case the rare earth ions were precipitated as the oxalate and then ignited to the oxide. The weights of the oxides were used to prepare exact normal solutions for the absorption spectrum measurements.

In the case of lanthanum, which has no absorption spectrum, the disappearance of the spectrum of the other rare earth was used to evaluate the purity of the lanthanum.

The ease and rapidity with which the absorption spectrum can be made, make the analysis of the rare earths a very simple problem. Standard chloride solutions of Nd⁺⁺⁺, Pr⁺⁺⁺, and Sm⁺⁺⁺, were employed. These solutions were used to determine the extinction coefficient for the said ions. Figure X shows the absorption spectrum for Nd⁺⁺⁺, Pr⁺⁺⁺ and Sm⁺⁺⁺ in 2N solutions and for a solution thickness of 2 cm. The absorption spectrums are shown in both the visible (tungsten filament) and in the ultra-violet (hydrogen lamp).

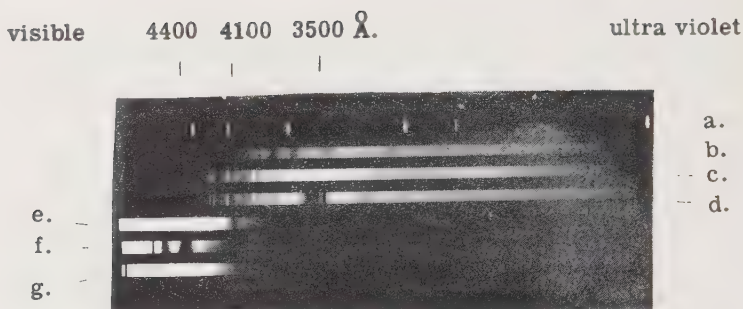


Figure X
Absorption spectrum of rare earth Chlorides

- a. This is the emission spectrum of mercury. This was used to determine the wave length.
- b. This is the absorption spectrum of Sm^{+++} in the ultra-violet. It should be noted that there are many absorption bands which are not very sharp.
- c. The absorption spectrum of Pr^{+++} , in the ultra-violet. Here only the hydrogen lines can be seen.
- d. This is the absorption spectrum of Nd^{+++} in the ultra-violet. Note the strong absorption bands in the region of $3500 \text{ \AA}$. These series of bands were used to determine the concentration of Nd^{+++} .
- e. Absorption spectrum of Sm^{+++} in the visible. There is a very strong absorption band in the region of $4076 \text{ \AA}$. This band was used to determine the concentration of Sm^{+++} .
- f. Absorption spectrum of Pr^{+++} . There are three very clear absorption bands. The third band (at $4440 \text{ \AA}$) was used for analysis.
- g. Absorption spectrum of Nd^{+++} in the visible. Only two narrow bands can be noted.

The fact that the principal absorption bands of these three rare earths are at different wave lengths allows one to make an analysis of the three rare earths even when they are together. This reality is very convenient and time saving.

Apparatus used

These first attempts to separate the rare earths were made with an apparatus 40 cm long. The apparatus was packed with 105 circular diaphragms. A voltage source of 600 volts was used. The countercurrent stream was controlled entirely by a conductivity cell in the cathode section. A rare earth concentration of about .18 N was employed. The concentration of the acetic acid in the countercurrent reservoir was maintained at .5 N. The apparatus was water cooled through its center. During the experiment, samples were taken (siphoned) from the cathode section for analysis. About 10 cc. of the rare earth solution was needed for an analysis. This corresponds to about 5 cm length of the apparatus or about 12% of the volume of the apparatus.

Table VI

<i>Separation of Rare Earths by Counter-current Electromigration.</i>			
<i>Voltage used</i>	<i>Mole % in Anode Section</i>	<i>Duration of Experiment</i>	<i>Mole % in Cathode Section</i>
600 V	La. 48 Nd. 52	120 hrs	99
600 V	La 27 Sm 25 Gd 25 Eu } Tb 23 Dy } Ho }	105 hrs.	99
600 V	Pr 82 Nd 18	150 hrs.	94 6
Cell Current		130 $\pm$ 10 ma	
Temperature		40 $\pm$ 5°C	
Diaphragms		105	
Tube length		40 cm.	

Results on the separation of rare earths with 600 volts

The results of the separation are given in table VI. In the first experiment La and Nd were mixed. The experiment went on for two weeks. After the first 120 hrs. daily samples of 25 mg were taken off the cathode section. The absorption spectrum showed no sign of Nd. The separated lanthanum oxide was white and gave a precipitate with oxalic acid in the presence of a large excess of hydrochloric acid.

As shown in table VI, the mixture of La and Nd used in the first experiment was 48 mole % La.

In the second experiment, a large number of rare earths were mixed together. The absorption lines of Sm and Gd were used to determine the purity of the product in the cathode section. The rare earth oxide obtained from the cathode section was pure white and contained no absorption lines at all. In the anode section, however, the 25% of Sm could be measured. The percent of Gd could also be measured. The presence of the other rare earths could be detected.

In the third experiment it was not possible to obtain an absolute separation of the two elements. After following the experiment for three weeks, a maximum of 96 mole % Pr was obtained. It is felt however, that with higher potentials it would be possible to carry out a complete separation of the two elements. The results of these three experiments are given in table VI.

Separation of a Pr, Sm mixture with 600 volts

From the conductivity curve of Spedding it can be expected that Pr would be concentrated in the cathode section.

The same apparatus was used as in the previous three experiments. A cell current of 130 ± 10 m.a. was used. The temperature of the electrolysis cell was held at 40 ± 5 C. Again 105 diaphragms were used in the packing. The results of this experiment are given in table VII.

Table VII
The absolute separation of Pr

Analysis of anode section Mole %	duration of	analysis of cathode section	Approx. rate at which 97% Pr can be taken from cathode section	Sol. conc.
48% Pr	160 hrs	98% Pr	15 mg/day	0.15N
18% Sm				
17% Gd				
17% { Eu				
{ Dy				
{ Tb				
{ Ho				

SEPARATION OF PR FROM A ND-PR MIXTURE

The results shown in table VI indicate that under the operating conditions, a potential of 600 volts was insufficient to bring about a clear cut separation of these two elements.

In this experiment, the separating process was repeated using a 2500 volt source. A separating tube 100 cm long and packed with 245 circular diaphragms was used. The initial rare earth mixture contained 82 mole % Pr and 18 mole % Nd. The operating conditions during the experiment are shown in table VIII.

Table VIII

Operating conditions in separating Pr from a Nd-Pr mixture with
2500 volts

Av. cell temp.	Av. cell current	Av. countercurrent stream volume	Volts/cm	Duration of experiment in hours
60 °C	105 m. a.	85 cm ³ /hrs.	24	150 hrs

The concentration of the rare earth solution was about .09 N. After the experiment had been carried out for 120 hrs. , 40 mg of the rare earths (as oxide) were taken for analysis from the cathode section. The absorption spectrum of the sample showed no traces at all of Nd. The analysis with respect to the Pr proved to be better than 98%.

As in the previous rare earth experiments, the acetate anion was employed. The concentration of the acetate solution was kept at about .3 N.

Approximation of the rare earth mobilities as related to electro-migration separations

If it is assumed, for the moment, that the separation of the rare earths cations is related only to the mobility of the ions, then equation no. 5 can be used to calculate the relative differential mobilities of two ions.

By using the results in the last series of experiments in conjunction with equation no. 5 (see page 13) the approximate ratio of the ionic mobilities can be calculated. The cell constant K" has already been evaluated and

is equal to .42 (see page 28). The results of these calculations are shown in table IX.

Table IX
Approximate ratio of the mobilities of the rare earth ions

Experiment no.	ions separated*	$\left(\frac{\mu_l}{\mu_h}\right)^{**}$ ratio of mobilities 400C
1.	La, Nd	1.1
2.	La, Sm***	1.16
3.	Pr, Nd	1.03
4.	Pr, Sm	1.07

* In the case where more than two ions have been used, it was assumed that the other ions behaved as Sm.

** These values have been calculated by using equation no. 5.

*** It was assumed that the distribution of the Pr and Nd in the separating tube followed the hyperbolic tangent law.

Conclusion on the rare earth mobilities from La to Sm

The calculated approximations shown in the table IX, indicate that the ionic mobilities of the four different rare earths vary from 3 to 16%. Corresponding values taken from the work of Spedding show that the mobilities vary from about .1 to .8%. The difference is enormous. No explanation can be given for this. It would be impossible to obtain an absolute separation of the rare earths under the given conditions if the differential mobilities of the ions had been so small as reported by Spedding. It is thought that possibly some other factor, such as complex ion formation with the acetate ion may be responsible for the large differential mobility observed in the electromigration process.

Conclusion on the separation of the elements from La to Sm

The foregoing experiments and results clearly show that the absolute separation of rare earths from La to Sm can be effectively carried out.

Although the results are very satisfactory, the fact still remains

that these results were probably not obtained under optimum conditions. It is felt that variations in the solvent, in the diaphragm packing, in the ionic concentration, or variations in the temperature of the experiment may help to bring about an even more rapid separation of the rare earths. The object of this work was not to find the optimum conditions for the separation of the rare earths, but rather to show that diaphragm counter current electromigration does work effectively and that it can be used to achieve an absolute separation of the rare earth ions.

THE CONCENTRATION OF CERTAIN RARE EARTH ELEMENTS IN THE TERBIUM GROUP

Materials used

A mixture of rare earths ranging from Sm to Ho has been used as the starting material. The mixture was received as the carbonate. An approximate analysis of this carbonate mixture has been made by using the absorption spectrum of the ions. The following approximation has been found.

Sm 35 weight % (evaluated by using a standard solution of pure Sm)

Eu 4% approximated by the extinction coefficient

Gd 30% approximated by using the extinction coefficient of Gd
from the literature see ref. (11)

Tb }
Dy } 31% obtained by difference
HO }

When this mixture was dissolved in HCl, brought to pH of 5, precipitated with oxalic acid and then ignited, the resulting oxide gave the following analysis:

Sm 42%
Eu 5 approx.
Gd 35% approx.
Tb }
Dy } 18% by diff.
HO }

It is thought that possibly the original carbonate mixture was precipitated by K_2CO_3 . Thereby precipitating complex rare earth potassium carbonates. The presence of potassium altered the percentage of rare earth present.

The colour of the ignited oxalate precipitate is a yellow-orange. The exact origin of this rare earth mixture is not known, except that the description accompanying the mixture stated that it should contain the rare earths only from Sm to Ho.

Procedure:

In the differential electromigration process for concentrating or separating ions, the faster ion is concentrated in the cathode section while the slower ion is concentrated in the initial solution reservoir. When a polynary mixture is used, then only two species of ions can be most effectively concentrated. The fastest and the slowest ions can be concentrated simultaneously. The in-between ions are found in the middle of the tube and are much more difficult to concentrate in the presence of the fastest and slowest ions. If the initial reservoir is large, then the increase of concentration of the slowest ion is hardly noticeable.

In order to follow through the change of the concentration of the slowest ion in the anode section, a special automatic evaporator was designed which maintained the anode volume at about 40 cm^3 . In this procedure, a relatively small amount of rare earths (about 500 mg) could be used to carry out the concentration. A sketch of the evaporator is shown in figure IX.

Two different experiments were designed to concentrate the fastest and slowest ions respectively. In the first experiment, the fastest rare earth ion was concentrated and a large initial solution reservoir was used. In the second experiment, the initial solution reservoir was maintained at 40 cm^3 by an automatic evaporator and the anode section of the separating tube was analysed for the slowest ion.

The concentration of the fastest ion in the cathode section

An initial mixture of rare earths with an approximate analysis given under materials was used. A circular pyrex tube 100 cm long with 245 diaphragms was used as the separating tube. A voltage of 2500 volts was available for the experiment. The volume of the initial anode reservoir was 2 liters, and 4.5 g of the initial rare earth mixture containing 42%

Sm_2O_3 was used. The operating conditions of this experiment are given in table X.

Table X
Operating conditions for the concentration of the
fastest rare earth ion

R. E. conc.	Av. cell temp.	Av. cell current	Av. countercurrent stream volume	volts/cm	Duration of experiment
0.08 N	45°C	100 m. a.	75 cm ³	24	6 weeks

It was possible to confirm the fact that neither Ce, Pr or Nd were present in the rare earth mixture, since even in the more concentrated solutions, no absorption spectrum could be detected for these ions. It was assumed that no lanthanum was present as the description accompanying the rare earth mixture clearly stated that the rare earths were lanthanum free, but this was not true. A considerable amount of lanthanum was soon found.

During the six week period the cathode section was analysed periodically by using the absorption spectrum. The analysis of the cathode section as a function of time is shown on table XI.

Table XI

Absorption spectrum analysis of the cathode section as function of time

Time in days	Mg of oxides taken from cathode section	% Sm in* sample	% Gd in** sample	% La in*** sample	Comments
0		42%	35%	-	Exp. started.
4	50 mg	0	0	99	No rare earth absorption bands could be detected.
5	45 mg	0	0	99	As mentioned above.
6	150 mg	60%	20%	-	The large sample was taken with the purpose of depleting the apparatus of La.
9	50 mg	0	0	99	
11	45 mg	0	0	99	
15	200 mg	58%	20%	-	Again a large sample was taken to attempt to remove all the La.

Table XI
(continued)

19	55 mg	73%	15%	-	
23	45 mg	85%	10%	-	
27	45 mg	93%	5%	-	In this absorption spectrum only faint bands could be detected for Gd.
31	210 mg	65%	15%	-	This large sample was taken to note the distribution curve of the Sm in the apparatus.
37	45 mg	85%	10%	-	
42	45 mg	90%	5%	-	The bands of Gd were quite faint.

* This analysis is correct to ± 1 . It was made by comparing the cathode section absorption band with that of a standard solution.

** This analysis is correct to ± 5 .

*** A white rare earth oxide which gave no absorption bands in the visible or in the ultra-violet absorption spectrum was assumed to be better than 99% La.

The unexpected presence of La in the rare earth mixture complicated the experiment considerably. Before the Sm could be concentrated, it was necessary to remove the last traces of La from the 4.5 gr. of the rare earth mixture. This explains the fluctuation of the percentage of Sm with the time.

The results of this experiment clearly show that Sm is the fastest rare earth ion of the terbium group. It is also obvious that La is faster than Sm, but this has already been shown.

The analysis are given in weight percent.

The concentration of the slowest ion in the anode section of the apparatus

Apparatus:

Again the rare earth mixture listed under materials was used. This experiment was designed to observe the anode section during the separating

process. In order to be able to detect a concentration shift in the rare earth cations in the anode section, the anode reservoir should be kept as small as possible.

An automatic evaporator has been designed, whereby the volume of the anode section can be controlled independent of the rate of liquid flow from the cathode section. Thus a constant volume can be maintained in the anode section at all times. The details of the evaporator are sketched in figure IX. The heat necessary to evaporate the water (also the acetic acid) from the anode section is supplied by alternating current going through the anodic solution in the evaporator. The resistance of the solution times the square of the current corresponds to the heat absorbed by the solution. If at any time the rate of evaporation is faster than the rate at which the water (dilute acetic acid solution) is fed into the apparatus, then the solution level in the evaporator falls below the platinum electrodes, and evaporation is automatically stopped. If however, the rate of evaporation is slower than the rate at which the water solution is added to the apparatus, then the solution level in the evaporator rises and supplementary contact is made with

*Automatic evaporator used in the experiment
for concentrating the slower ion.*

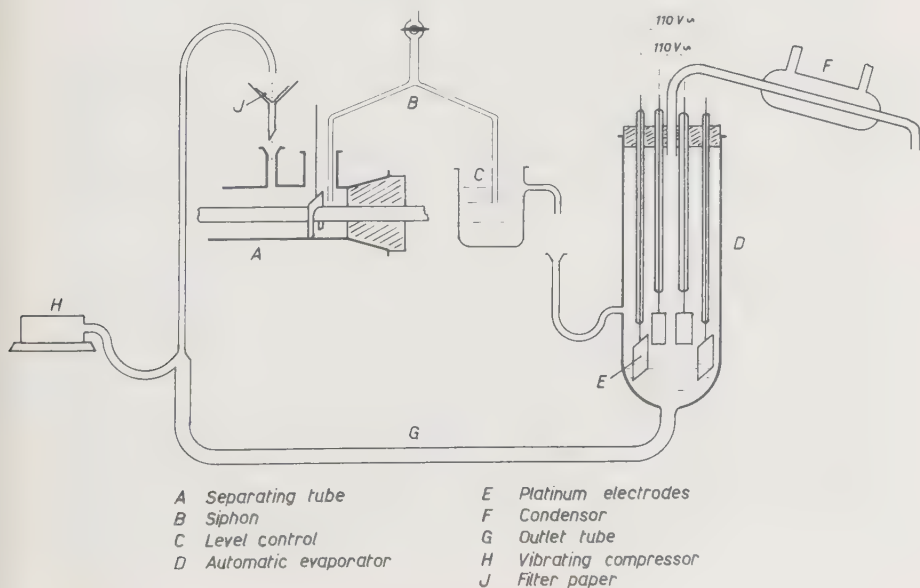


Figure IX

the two higher platinum electrodes. Under these conditions the rate of evaporation is about double that of the previous rate. Of course, the small evaporator is well insulated with felt and asbestos to avoid excessive heat losses to the surrounding.

In order to keep the evaporator and the anode section of the separating tube at the same concentration and composition, an airlift pump was placed between the evaporator and the anode section. A vibrating compressor (the type used to supply air to fish aquarium installations) was used as a means of operating the lift pump.

Much caution is to be taken in the circulation of the solution from the evaporator to the anode section. When working with 2500 volts, a short circuit by way of the evaporator lines is inevitable, if the circulation is not interbroken by an airspace of at least 10 cm. The circulating solution is allowed to drop through the 10 cm airspace, thus avoiding a possible short.

Procedure:

One gram of the mixed rare earth oxides were taken for this experiment. Five hundred mg were needed in order to prepare the solution in the separating tube. The remaining 500 mg were placed in the evaporator. A separating tube 110 cm long, packed with 260 circular diaphragms was used. A potential of 2500 volts was employed across the apparatus.

Although it is the anode section that is to be observed most closely in this experiment, the rare earths must still be removed from the cathode section in order to allow the slowest ions to gradually accumulate in the anode section. After most of the extra ions have been removed from the cathode section, then an analysis of the anode section will show what has happened.

During the first five days of operation, no samples were taken from the apparatus. On the sixth day, 40 mg (as oxide) were taken from the cathode section. Of course, in turn, 40 mg of rare earths in the evaporator were pushed into the apparatus, thus maintaining the apparatus in its normal condition. For the next 8 days, about 40 mg of the rare earths were taken daily from the cathode section. The experiment was then allowed to continue for five more days without sampling. After a total of 18 days, the contents of the evaporator (80 mg) were analysed. The sample showed less than 15%

Sm. The colour of the oxide was a brownish yellow, indicating an increase in the concentration of Tb. The absorption lines of Gd, could still be detected very clearly. The operating conditions of the experiment are shown in table XII.

Table XII
Operating conditions for concentrating the slowest ion

Conc. of the R. E. solution	Temp. of the separating cell	Av. cell current	Volume of the countercurrent stream	Duration of experiment
0.06 N	37° C	90 m. a.	57 cm ³ /hr	18 days

The dilute acetic acid solution (.3 N) condensed from the evaporator was returned to the countercurrent reservoir.

CONFIRMING THE SHIFT IN THE CONCENTRATION OF THE TERBIUM EARTHS BY MEASURING THE MAGNETIC SUSCEPTIBILITY OF THE IONS

The simplest method to determine the magnetic susceptibility of a solution is to suspend the solution in a uniform magnetic field and to measure the force exerted on it by the field. In the following determinations, one half cm³ of a solution contained in a .2 cm (inside diameter) glass tube was suspended in a magnetic field. This tube was suspended from an arm of a balance. The difference in weights before the magnetic field was switched on, and after it was switched on, was recorded as the pull due to the magnetic field. The strength of the magnetic field used was in the neighborhood of 15'000 ampere turns. Results of these measurements are given in table XIII.

The literature shows that the magnetic moments of the rare earths from Sm to Ho increase almost in a linear manner. The measured magnetic moment for Sm is 1.6 Bohr magneton, while that of Ho is 10.6.

It is thus clear that rare earths concentrated in the anode section are richer in the elements near Ho, than are the rare earths which were concentrated in the cathode section.

Table XIII

Measurements of the magnetic susceptibility of the concentrated rare earths

Solutions tested	Concentration of the solution	Pull caused by * the magnetic field	Comments
Distilled water		- 20 mg	Water is diamagnetic
Rare earths concentrated in the anode section	1.5 N	+ 98 mg	
Initial rare earth mixture	1.5 N	+ 61 mg	
Rare earths concentrated in the cathode section	1.5 N	+ 31 mg	

* The sensitivity of the balance was 1 mg.

CONCLUSION ON THE CONCENTRATION AND SEPARATION OF RARE EARTHS BY COUNTERCURRENT ELECTROMIGRATION

1. The absolute separation of the rare earths from La to Sm inclusive can be effectively carried out by countercurrent electromigration.
2. The rare earths with the lower atomic weight migrate faster than the rare earths with a higher atomic weight.
3. The relative differential mobility of the rare earths from Sm to Ho is very much smaller than the relative differential mobility of the rare earths from La to Sm.
4. Even with the voltage source of 2500 volts we did not yet achieve an absolute separation of the rare earths from Sm to Ho under the conditions of the foregoing experiments.
5. Considerable enrichments of the rare earths from Sm to Ho can be achieved by countercurrent electromigration.

CONCENTRATION OF ^{85}Rb AND OF ^6Li . IN AN AQUEOUS MEDIUM

Theoretical considerations

It has already been mentioned that the separation process of electro-migration is based upon the difference of the ionic (hydrated) weights rather than on the difference of the atomic weights of the isotopes.

E. W. Washburn in 1909 (18) by using sugar refinoase as a reference substance was able to measure the relative water of hydration of the alkali metal ions. However, his method of measurement was such that he was obliged to assume the hydration number of the chlorine ion. He assumed two values for the water of hydration of chlorine, and calculated the corresponding values for the alkali metal ions. His results are given in table XIV.

Table XIV
Hydration numbers of the alkali metals

Cl^-	H^+	Li^+	Na^+	K^+	Cs^+
4 (assumed)	1	14	8.4	5.4	47
9 (assumed)	2	25.3	16.6	10.5	9.9

By interpolating table XIV, the corresponding values for the hydration number of rubidium are found to be 5 and 10. It is arbitrarily assumed that the higher values of the hydration numbers are the correct ones. It is further assumed that both isotopes of each metal ion are equally hydrated. Under these assumptions, the calculated ratio of the isotopic mobilities in water are given below.

$$\frac{\mu_{^{85}\text{Rb}^+}}{\mu_{^{87}\text{Rb}^+}} = \sqrt{\frac{^{87}\text{Rb}^+ \cdot 10 \text{ H}_2\text{O}}{^{85}\text{Rb}^+ \cdot 10 \text{ H}_2\text{O}}} = 1.0038$$

$$\frac{\mu_{^6\text{Li}^+}}{\mu_{^7\text{Li}^+}} = \sqrt{\frac{^7\text{Li}^+ \cdot 25 \text{ H}_2\text{O}}{^6\text{Li}^+ \cdot 25 \text{ H}_2\text{O}}} = 1.0011$$

Results on the concentration of ^{85}Rb

A pyrex separating tube one meter long was used. The tube was packed with 260 circular diaphragms. The electrolysing solution contained the rubidium as the hydroxide. The concentration of the rubidium was .006 N. A potential of 2300 volts were used (see page 25).

The control of the countercurrent stream was divided. Instead of having to conductivity cell in the cathode section completely steer the stream, it was allowed to steer only about half of the countercurrent stream. The other half of the steering was regulated by the separating cell current. The pressure cells from both steering sections were placed in parallel. It was observed that such divided control was more uniform, and responded more sensitively to the changes of the day and evening voltages. The operating conditions of the concentration of rubidium isotopes are shown in table XV.

Table XV

Av. cell current	Ab. temperature	Av. countercurrent streamt
110 m.a.	80° C (1st week)	280 cm ³ /hr.
	40° C (thereafter)	190 cm ³ /hr.

The rubidium used was C. P. grade, bought as the chloride. After the experiment ran for one week, an analysis was made of the cathode section. The larger part of the ions there were cesium. The presence of cesium was also confirmed by the use of silico-tungstenic acid.

The solution which left the anode section was boiled to drive off the excess water and then it was fed back to the anode reservoir.

The experiment was run for 8 weeks. During the first week the apparatus was kept at an average temperature of 80° C. For the remaining 7 weeks the average temperature was maintained at 40° C. The first sample was taken off after 8 days of operation. The sampling was done by pipetting 8 cm³ of solution off the cathode section. The 8 cc corresponded to about 5 mg of RbCl. The 8 cc also correspond to about 5 cm of tube length. On the next day 8 more cc were taken from the cathode section. The position of this sample, however, is not at the cathode but really about 5 cm from

the cathode since the first sample corresponds to the cathode section. The results of the concentration are shown in table XVI.

Table XVI
Concentration of ^{85}Rb

Time after exp. was started	Position of sample in the separating tube	% ^{85}Rb
0	cathode section	72.22
8 days	cathode section	73.82
9 days	5 cm from cathode section	73.61
35 days*	cathode section	73.62

* Sampling was started after 21 days of operation. During the following 24 days 1 cc was taken from the cathode section each day. The 24 cc were then sampled as one unit. The average time is recorded as 35 days.

Table XVI indicates that the separation after one week is better than the separation after 5 weeks. Only one possible explanation can be given for this. During the first week the temperature of the separating cell was maintained at 80°C . while during the following weeks the average temperature of the cell was kept at 40°C . The possibility that the hydration of the rubidium ion is smaller at the higher temperature can well account for the better separation found at the higher temperature.

The concentration of ^6Li

Details:

In the experiment for the concentration of ^{85}Rb , the largest part of the current was transported by the hydroxide ion. As a result of this it was necessary to work with very dilute solutions. In the case of lithium the problem becomes even more marked. To remedy this, the acetate anion has been used in the concentration of ^6Li . For the sake of safety the acetate concentration in the countercurrent reservoir was kept twice that of the lithium in the apparatus.

The apparatus used was a pyrex tube, 75 cm long and packed with 210 diaphragms. Again the control of the countercurrent stream was divided.

The concentration of lithium in the apparatus was about 0.007 N. The operating conditions in this experiment are given in table XVII.

Table XVII
Operating conditions during the concentration of ${}^6\text{Li}$

Anode cathode distance	Av. cell current	Voltage	Av. temperature	Av. counter-current flow
75 cm	90 m. a.	2300	41° C	140 cm ³ /hr.

Lithium is the slowest alkali-metal cation. It was anticipated that any impurities in the lithium would accumulate in the cathode section. Chemically pure lithium hydroxide was used as a source of lithium. After one week of operation, the analysis of the cathode section showed 80% potassium, 15% sodium and 5% lithium. Even after 3 weeks of operation, traces of sodium (5%) were still found in the cathode section. It was assumed that this sodium came from the glass ware which was constantly in contact with the solution and might have performed a certain ion exchange. The same lithium was recycled during the experiment.

Results on the concentration of ${}^6\text{Li}$

The experiment was run for 6 weeks. After three weeks sampling at the cathode section was started. Each day 2 cc of solution were taken off the cathode section. This was continued for three more weeks. The analysis of the sample obtained over a period of 3 weeks are shown in table XVIII.

Table XVIII
Concentration of ${}^6\text{Li}$

Time	Position in the separating tube	% ${}^6\text{Li}$
0	In cathode section	7.31
4.5* weeks	In cathode section	7.61

* This is an average time. The sampling was started after three weeks, and terminated after 6 weeks. About 80 mg of LiCl were obtained in these three weeks.

CONCENTRATION OF ^{39}K

Details:

The experience obtained from the concentration of ^{85}Rb indicated that the concentration of the lighter isotope was better when the temperature of the separating tube was near 80°C . This experiment was designed especially to work at a temperature above 80°C .

A pyrex separating tube 75 cm long and packed with 210 circular diaphragms was used for the concentration. Here again the acetate anion was used instead of the hydroxide anion. The operating conditions during the experiment are given in table XIX.

Table XIX
Operating conditions during the concentration of ^{39}K

Anode-cathode distance	Av. cell current	Av. cell temperature	Volts/cm	Av. countercurrent stream volume
75 cm	110 m. a.	85°C	30	$260\text{ cm}^3/\text{hr.}$

The countercurrent stream was automatically controlled in part by conductivity cells and in part by the cell current itself.

The experiment was carried out for 20 days before sampling was started. After 20 days 4 cm^3 were taken from the cathode each day for the following 6 days. The experiment was then stopped. About 15 mg of the potassium as the chloride is the equivalent taken out in the 6 days.

No analysis has yet been received for this experiment. The concentration of the potassium acetate solution in the apparatus was about .006 N.

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Curriculum vitae

I was born on the 21 of March 1923 in Monterrey, Mexico. I attended and completed grammar school in Chicago, Illinois. In the spring of 1937 I enrolled in the Chicago Public High School. My high school education was terminated in 1941 and the same year, I had started to study chemical engineering at the University of Missouri, Columbia, Mo. During World War II, my studies were interrupted for two years. From 1943 to 1945, I served in the Armed Forces. I continued my studies after the war and received a B.S. degree in chemical engineering in 1947. Previous to this, I have also studied at the University of Mexico, Mexico, and at the University of Rhode Island, Rhode Island (U.S.A.).

In the fall of 1947, I was enrolled at the University of Montreal, Montreal, Canada, where I have received the masters degree (magna cum laude) in chemical engineering in 1948. The title of my masters degree dissertation was: "The mechanisms of corrosion of ferrous metals, and the use of inorganic inhibitors." This dissertation was carried out under the supervision of Prof. Roger Brais.

From 1948 to 1950 I was employed as a research chemist by General American Transportation Corporation at East Chicago, Indiana. During my stay with the company, I have obtained one U.S. patent in physical chemistry. I was employed by Armour and Co. from 1950 to 1951 as a research physical chemist. Here I have obtained two more U.S. patents. During the period of 1951 to 1953, I have been working on the doctor's dissertation at the University of Zürich, under the able leadership of Prof. K. Clusius.

